Dielectric Relaxation of Liquid Polyethyleneglycol on Addition of Polyvinylpyrrolidone

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The set of relaxation times describing the dynamic dielectric properties of liquid polyethyleneglycol 200 at 20 and 40 °C is found to be practically independent of the admixture of polyvinylpyrrolidone, though the viscosity is appreciably increased. This is compared to the rather similar behaviour of small molecular solvents.

In previous dielectric relaxation studies [1–3] we have found that the behaviour of a polar solvent with polymer solutes differs remarkably from that with low molecular solutes: Depending on polymer concentration, two spectral components are revealed which *both* are ascribable to the *solvent*. Their relaxation times stay nearly independent of the concentration, although the viscosity may be increased considerably. The assumption of microheterogeneity is adequate to explain these relaxation contributions, distinguishing portions of unaffected bulk solvent from portions which are slowed down in their relaxational motion as a result of some kind of polymer 'solvation'. That behaviour was observed similarly with aprotic [1–3] as well as protic solvents [1], in any case with solvents which consist of relatively small molecules.

It seemed worthwhile to extend these observations to solvents consisting of larger molecules such as oligomeric liquids, in order to see to what extent the apparent 'decoupling' of relaxational behaviour and macroscopic viscosity may persist. The present note reports results obtained with polyethyleneglycol (PEG) as solvent and (as in the above-mentioned work) polyvinylpyrrolidone (PVP) as polymeric solute. The mean relative molar mass of PEG used was $\bar{M}_r \approx 200$, that of PVP was 24 000. The highest concentration studied corresponds to a mass fraction $w_{PVP} = 0.13$. Some results for related systems will be mentioned for comparison.

Chemicals from Aldrich were used as obtained. The imaginary part $\varepsilon''(\omega)$ of the dielectric function (viz. the dielectric loss) was measured with an uncertainty of a few percent at 12 spot frequencies ranging between about 10 MHz and 36 GHz at two temperatures, 20 and 40 °C. The viscosity shall serve only for qualitative orientation, it was measured with an Ostwald viscosimeter.

On addition of PVP, the well known $\varepsilon''(\omega)$ spectrum of pure liquid PEG, which is broader than a Debye curve [4, 5], is gradually shifted towards lower frequencies. Closer inspection shows that also the shape is slightly altered. For a formal description we have fitted a sum of Debye type functions to the data,

$$\varepsilon''(\omega) = \sum S_i \frac{\tau_i \, \omega}{1 + \tau_i^2 \, \omega^2}. \qquad (1)$$

While for pure PEG three spectral components C_i are sufficient, the solution spectra, at least for higher PVP concentrations, are clearly better fitted by four terms (this reduces the rms relative deviation by a factor of $2 \div 3$ in comparison to a three term fit). The relaxation parameters τ_i and S_i as obtained in the latter way (pronouncing moreover the relaxation strength S_2 if possible within its variability range) are represented in Figure 1. The temperature dependence may be expressed by an activation enthalpy ΔH_τ according to an Arrhenius law. For the main term there is on average $\Delta H_{\tau 2} \approx 22$ kJ/mol.

The four term fit scheme by itself yields relaxation times $\tau_1 \ldots \tau_4$ which stay approximately constant, independent of concentration and, consequently, viscosity. The viscosity increases almost exponentially from $\eta = 62.8$ mPas for pure PEG to 568 mPas (at 20 °C) for the highest concentration ($w_{PVP} = 0.13$).

Since the inference that relaxation times do *not* change as the viscosity is influenced by the choice of the fitting scheme, it may be supported by a further example. Using the protic polymeric solute polyacrylic acid (PAA), as high viscosities as mentioned
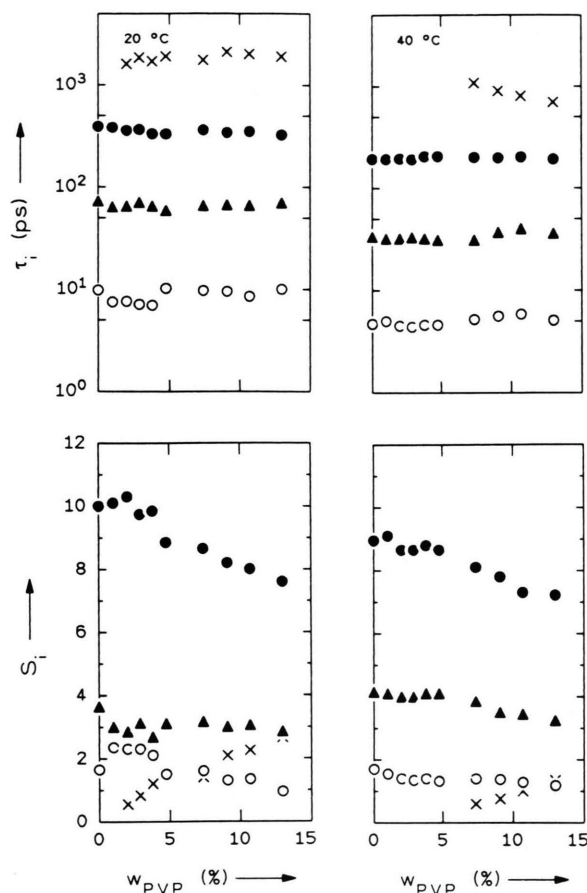
Fig. 1. Relaxation parameters τ_i and S_i according to (1) for PEG 200 + PVP, 20 °C (left) and 40 °C (right). Spectral components C_i: $\times\, C_1$, $\bullet\, C_2$, $\blacktriangle\, C_3$, $\circ\, C_4$.

before are achieved already at rather low PAA content. With $w_{PAA} = 0.01$ one obtains $\eta = 550$ mPas at 20 °C. At such a low concentration the polar solute itself is unlikely to be *directly* discernible in the dielectric absorption spectrum. Notwithstanding the increased viscosity, the spectrum appears practically unaltered to within experimental uncertainty, which means constancy of relaxation times.

Turning to the PVP/PEG system again, let the assignment of the spectral components C_i (Fig. 1) be briefly discussed. From the unaltered relaxation times $\tau_2 \dots \tau_4$ as well as from that the concentration dependence of $S_2 \dots S_4$ it is evident that these spectral components are essentially ascribable to the solvent PEG. Component C_1, on the other hand, might be due to 'affected' PEG and/or to the solute PVP. An attempt at its assignment shall be made by comparison with our previous results.

With low molecular solvents (even with ethanediol [1], a liquid similar to PEG with respect to the OH functionality) the PVP contribution to the overall absorption is found to be very broad, reaching down to some MHz, in contrast to the C_1 component of the present examples. Assuming for the moment that C_1 comprises the total PVP contribution, one expects from the comparative examples that the relaxation strengths S_1 be greater than observed (e.g. for $w_{PVP} = 0.13$, 20 °C, expected: $S_1 \gtrsim 3$, experimental: $S_1 \approx 2.5$). From this and the finding mentioned first it follows that the contribution of PVP to the dielectric spectra of the present solution differs qualitatively from that when dissolved in low molecular liquids, probably because of interferences with the PEG relaxation which may alter the structural and dynamical circumstances of PVP. Thus, $C_2 \dots C_4$ may include some minor PVP contributions. The spectral component in question, C_1, is likely to be essentially due to the solute PVP.

Our interest concerns the solvent rather than the solute. The inference that this is characterized by the spectral components $C_2 \dots C_4$ implies the peculiarity that, in spite of increasing viscosity, the relaxation of a considerable portion of the solvent stays apparently unaffected by the polymeric solute, with that resembling low molecular solvents. In contrast, however, the remaining part of the spectrum cannot further be separated into contributions from solute and 'affected' solvent. Comparable results obtained with PEG 400 are informative in that respect. In the case of this solvent, arguments in favour of the four term fit are less compelling, hence different solvent and solute contributions are hard to distinguish at all. In conclusion, PEG 200 seems to take an intermediate position between low molecular and higher polymeric solvents with regard to the appearance of dielectrically discernible contributions which can be pictured by a two state (affected vs. bulk solvent) model.

[1] E. Dachwitz, Z. Naturforsch. **45a**, 126 (1990).
[2] M. Rohmann, E. Dachwitz, and M. Stockhausen, Colloid Polym. Sci. **268**, 326 (1990).
[3] M. Rohmann and M. Stockhausen, Z. Naturforsch. **46a**, 1001 (1991).
[4] M. Davies, G. Williams, and G. D. Loveluck, Z. Elektrochem. **64**, 575 (1960).
[5] E. Wessling, M. Stockhausen, and G. Schütz, J. Molec. Liq. **49**, 105 (1991).